A method employing STM for the estimation of relative changes in the work function of modified metal tips

R B SHARMA[†], C P VINOD and G U KULKARNI*

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India
[†]INS Shivaji, Lonavla 410 402, India

Abstract. *I–z* spectroscopy measurements using a scanning tunnelling microscope (STM) were carried out to determine the change in the work function of a W tip following one monolayer (1 ML) deposition of Ni and subsequent annealing at 700 K. The variation in the actual gap voltage obtained from the *I–z* data of the clean tip was used in the calculation. The estimated values of the change in work function, 0·16 eV and 0·59 eV, for as-deposited and annealed tips, respectively match closely with the reported values. The method is generally applicable to chemically modified metal tips.

Keywords. *I–z* spectroscopy; scanning tunneling microscope; workfunction.

1. Introduction

Surface modification at nanoscale of metals and semiconductors is important for a variety of applications in the field of microelectronics. Field emission devices for example, employ tips that have been subjected to physical and chemical procedures to improve the performance. Local properties such as work function, change following such modifications and it is indeed crucial to monitor and control the changes in order to arrive at desired properties. Field emission microscope (FEM) has been used in many cases to detect changes in the work function of a variety of metal tips following gas adsorption (Gomer 1961) and metal deposition (Joag and Jones 1984; Sidorski 1984; Gotoh *et al* 1996; Nagao *et al* 1996; Sharma *et al* 1998). This method uses high tip-anode voltages of the order of kV to achieve electron emission. The current trend in technology, however, demands the measurements to be carried out at low voltages.

We have explored the possibility of determining the changes in the work function following tip modification by tunneling measurements under low voltages using a STM set up. STM offers a high-resolution probe to measure local work function variations caused by subtle changes of the tip surface. The experiment involves measurement of the tunnel current, I, as a function of the tip-sample distance, z, under a given bias voltage of V. The local work function (f) is related to the gap conductance, G, as follows (Bonnell 1993)

$$f = 0.952 \times (\mathrm{d}\ln G/\mathrm{d}z)^2. \tag{1}$$

Studies using STM mostly concentrate on work function measurements of metal surfaces. Jia *et al* (1998) determined the variations in the local work function at the steps on Cu(111) and Au(111) surfaces. Clarke *et al* (1996) studied the tip-surface interactions in the case of W tip/Cu(100) surface. Using a W tip, Olesen *et al* (1996) measured the apparent barrier height at Au(110), Pt(100) and Ni(100) surfaces by measuring the tunnel current and voltage simultaneously. They showed that for a reliable estimation of the gap conductance from an *I–z* measurement, it is necessary to consider the variations in the gap voltage as well.

We have found an alternative procedure to measure the relative changes in the work function of a metal tip employing STM in the default d.c. mode. The *V–z* variations are derived using (1), based on the known work function of the clean tip

$$(\mathrm{d}\ln V/\mathrm{d}z)_{\mathrm{clean}} = (\mathrm{d}\ln I/\mathrm{d}z)_{\mathrm{clean}} + \sqrt{f_{\mathrm{clean}}}. \tag{2}$$

The gap conductance after tip-modification is estimated assuming that the circuit characteristics remain similar.

$$(\mathrm{d}\ln G/\mathrm{d}z)_{\mathrm{modified}} = (\mathrm{d}\ln I/\mathrm{d}z)_{\mathrm{modified}} - (\mathrm{d}\ln V/\mathrm{d}z)_{\mathrm{clean}}. \tag{3}$$

The relative change in the work function is then expressed as

$$\Delta f = f_{\mathrm{modified}} - f_{\mathrm{clean}}. \tag{4}$$

This method was tested using a Ni modified W tip in a UHV STM set up. The measured values of the work function of as-deposited and annealed tips have been found to be in agreement with the reported ones.

*Author for correspondence

2. Experimental

Scanning tunnelling measurements were carried out on a UHV STM Omicron Vakuumphysik instrument. The W tips were prepared by electrochemical etching and were stored in UHV. A freshly cleaved highly oriented pyrolytic graphite (HOPG) surface was used as the substrate. The STM images of the graphite were first obtained to check the quality of the tips. For the spectroscopic measurements, the tip was positioned on a large flat terrace on the substrate away from the steps. A constant bias voltage of 91 mV was applied to the sample with the tip at ground potential. A set current (I_{set}) of 10 nA was used. The feedback loop was temporarily disabled and a voltage ramp was superimposed on the reference of the feedback for achieving a controlled movement of the tip along the z-axis with respect to initial position ($z = 0$). Initially, the tip was moved by 9 Å towards the surface ($z = -9$ Å) and then the variations in the tunnel current, I, were recorded while retracting from the substrate with z varying from -9 Å to $+10$ Å at 200 data points with an acquisition time of 400 μs at each point and a delay of 2000 μs between two consecutive measurements. The speed of the tip was set at 500 nm/s.

The $I-z$ measurements were first performed with a clean W tip in UHV. *In situ* deposition of high purity nickel (99·99%, Aldrich) on W tip was done by resistive evaporation. A coverage of ~ 1 monolayer was obtained based on a calibration done using XPS measurements on a graphite surface with an identical Ni coverage (Seah and Dench 1979). The $I-z$ spectroscopy measurements were repeated on the as-deposited tip. The tip was then annealed in UHV at 700 K for 300 s. The quality of the HOPG image was also improved following annealing. $I-z$ measurements were then performed on the annealed tip under similar conditions.

3. Results and discussion

Figure 1a shows the $I-z$ characteristics of a clean W tip obtained with a gap voltage of 91 mV and a set current (I_{set}) of 10 nA. In the advanced position ($z = -9$ Å), the tunnel current is ~ 13 nA and it decreases rapidly to 6 nA in the retracted mode at $z = +10$ Å. We notice that while passing through initial position ($z = 0$), the current is slightly less (~ 8 nA) than the I_{set}. In order to extract the actual gap voltage variations during the $I-z$ measurement, we calculated ln$I$ for various z values (figure 1b). Assuming that $f_W = 4·54$ eV, we obtained $(\mathrm{d}\ln V/\mathrm{d}z)_{clean}$ from the slope of the linear fit shown in figure 1b using (2).

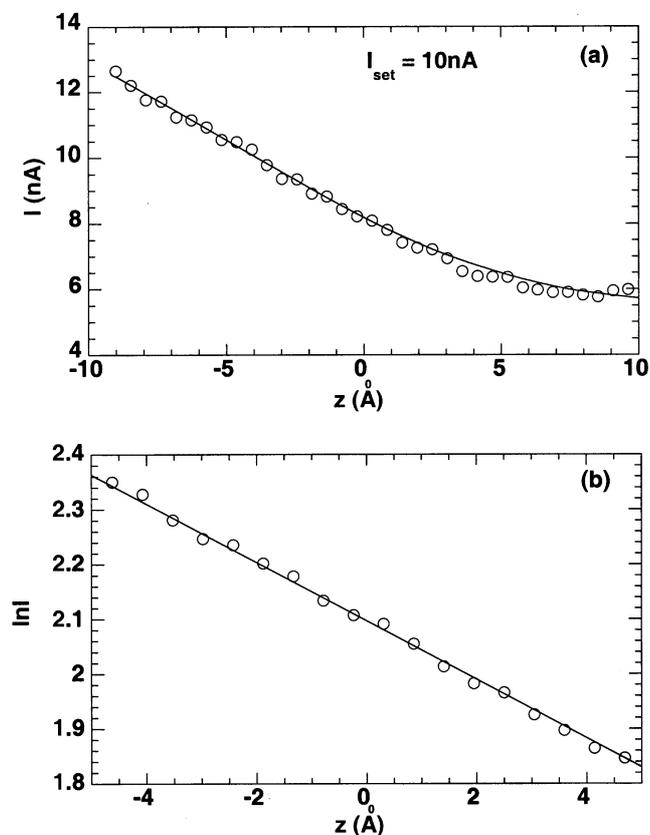**Figure 1.** (**a**) Variation in the tunnel current, I, with tip-sample separation, z and (**b**) that of ln$I$ with z.
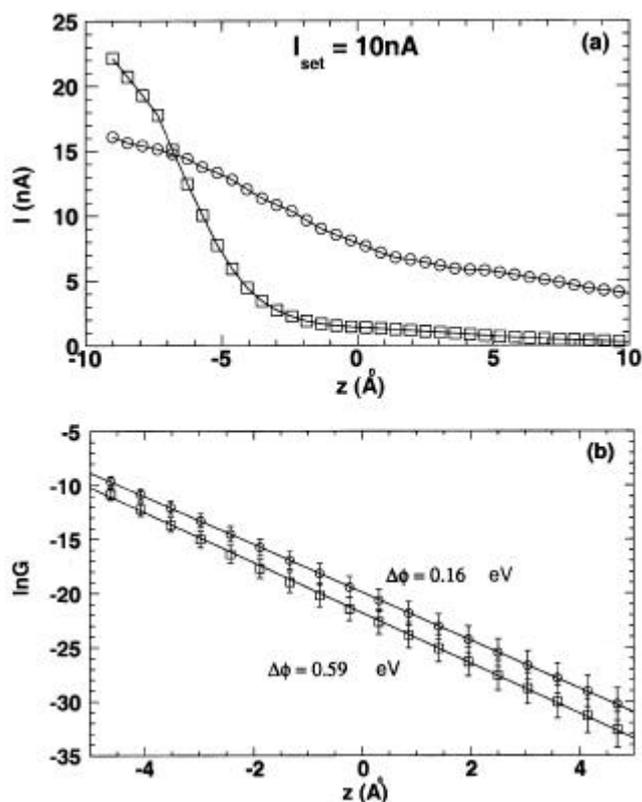

Figure 2. Variations in the tunnel current, I, (**a**) and ln$G$ (**b**) with tip-sample separation, z; as-deposited, circles; annealed, squares.

In figure 2a, we show the I–z characteristics for the deposited and annealed tips. We observe that in the case of as-deposited tip, the current starts from ~ 16 nA at $z = -9$ Å and decreases gradually to a value of 4 nA at $z = 10$ Å while in case of the annealed tip, the current starts at ~ 22 nA and decreases rapidly to zero at higher distances. The enhancement in the tunnel current arises due to the new states near tip apex (Bonnell 1993).

The value of $(\mathrm{d}\ln I/\mathrm{d}z)_{\mathrm{modified}}$, obtained from the respective I–z characteristics was substituted in (3) to calculate $(\mathrm{d}\ln G/\mathrm{d}z)_{\mathrm{modified}}$. This provided the estimation of the work function of the modified tip. However, the values obtained rely on the conditions employed for the clean tip and therefore, only the relative change and not the absolute value of the work function is to be taken seriously. Using (4), we obtained Δf of $+0.16$ and $+0.59$ eV for as-deposited and annealed tips, respectively. In order to validate our method, we calculated $\ln G$ values from $(\mathrm{d}\ln I/\mathrm{d}z)_{\mathrm{modified}}$ in both the cases and obtained linear variations with z as expected (Bonnell 1993; Olesen *et al* 1996) (see figure 2b).

An earlier study from this laboratory using XPS measurements (Kulkarni and Vinod 1997) has shown that the binding energy of $2p_{3/2}$ core-level of nickel deposited on a polycrystalline tungsten surface shifts by ~ $+0.15$ eV for a metal coverage of one monolayer. This enhancement was attributed to a charge transfer process across the Ni/W interface leading to an increase in the work function. The present finding of the change in the work function of the as-deposited tip agrees well with the XPS study. Also, the change in the work function obtained in the case of annealed tip ($+0.59$ eV) is quite comparable with that from a field emission study ($+0.52$ eV) (Sharma *et al* 1998).

We have used several sets of bias voltage and set current in order to ascertain their influence on the work function measurements. For lower value of I_{set} (~ 1 nA), the estimated values of the work function were found to be similar to that at 10 nA. At higher I_{set} value of 20 nA, the values were significantly lower, probably due to induced polarization at relatively smaller tip-sample separations. However, the measurements were not very sensitive to the changes in the bias voltages.

References

Bonnell D A 1993 *Scanning tunneling microscopy and spectroscopy. Theory, techniques and applications* (New York: VCH)

Clarke A R H, Pethica J B, Nieminen J A, Basenbacher F, Laegsgaard E and Stensgaard I 1996 *Phys. Rev. Lett.* **76** 1276

Gomer R 1961 *Field emission and field ionization* (Harvard, Cambridge, MA: Harvard University Press)

Gotoh Y, Nagao M, Matsubara M, Inoue K, Tsuji H and Ishikawa J 1996 *Jpn J. Appl. Phys.* **35** L1297

Jia J F, Inoue K, Hasegawa Y, Yang W S and Sakurai T 1998 *Phys. Rev.* **B58** 1193

Joag D S and Jones J P 1984 *J. Phys.* (*Paris*) **C9** 59

Kulkarni G U and Vinod C P 1997 *Appl. Surf. Sci.* **115** 336

Nagao M, Matsubara M, Inoue K, Gotoh Y, Tsuji H and Ishikawa J 1996 *Jpn J. Appl. Phys.* **35** 5479

Olesen L, Brandbyge M, Sorensen M R, Jacobsen K W, Laegsgaard E, Stensgaard I and Besenbacher F 1996 *Phys. Rev. Lett.* **76** 1485

Seah M P and Dench W A 1979 *Surf. Interface. Anal.* **1** 2

Sharma R B, Yawalkar P W, Pradeep N and Joag D S 1998 *Ultramicroscopy* **73** 99

Sidorski Z 1984 *Appl. Phys.* **A33** 213